Proposed Orbital Ordering in MnV_2O_4 from First-principles Calculations

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Based on density functional calculations, we propose a possible orbital ordering in MnV_2O_4 which consists of orbital chains running along crystallographic a and b directions with orbitals rotated alternatively by about $45°$ within each chain. We show that the consideration of correlation effects as implemented in the local spin density approximation (LSDA)+U approach is crucial for a correct description of the space group symmetry. This implies that the correlation-driven orbital ordering has a strong influence on the structural transitions in this system. Inclusion of spin-orbit effects does not seem to influence the orbital ordering pattern. We further find that the proposed orbital arrangement favours a noncollinear magnetic ordering of V spins, as observed experimentally. Exchange couplings among V spins are also calculated and discussed.

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The spinel compounds with a chemical formula of AB_2X_4 where B sites are usually transition metal ions, form a frustrated pyrochlore lattice with corner-sharing tetrahedra. These compounds show a complex behavior including structural transitions from cubic to tetragonal symmetries which are often accompanied by an orbital order-disorder transition as well as complicated magnetic orderings at low temperatures[1].

The spinel MnV_2O_4 has experienced a recent surge in activities due to new experimental observations in single crystals[2] revealing a lower symmetry structure than previously suggested[3]. This has important implications for the related orbital order at low temperatures which is still unclear. The presence of two magnetic ions in MnV_2O_4 (Mn with spin 5/2 and V with spin 1) translates into more complex magnetic phase transitions in this system than in other vanadium spinel oxides such as ZnV_2O_4, MgV_2O_4 or CdV_2O_4 with nonmagnetic A-site ions. Recent experimental findings[2,4] indicated that MnV_2O_4 undergoes a phase transition from paramagnetic to a collinear ferrimagnetic phase at 56K where the Mn and V spin moments point in opposite directions. At T = 53K a second magnetic phase transition to noncollinear ferrimagnetism follows accompanied by a structural transition from cubic to tetragonal phase.

The cubic to tetragonal structural transition in MnV_2O_4 is, similar to other vanadium spinels, associated with a compression of the VO_6 octahedron ($c_T/a_T = 0.98$). The octahedral environment of V (VO_6) splits the d states into lower t_{2g} and higher e_g. Since V^{+3} is in a $3d^2$ configuration, the t_{2g} orbitals are partially filled and possible orbital orderings may occur. Earlier experimental observations[3] indicated the tetragonal space group to be $I4_1/amd$. However, recent precise measurements on a single crystal[2,4] showed that the tetragonal space group is $I4_1/a$. Since the orbital order and, accordingly, the magnetic order are closely related to the underlying space group symmetry, it is very important to establish the space group symmetry unambiguously.

The $I4_1/a$ space group breaks the mirror and glide symmetries present in the $I4_1/amd$ space group, which implies that two of the four V-O bonds in the ab plane are shorter whereas in $I4_1/amd$ symmetry all four V-O bond lengths are the same. Garlea *et al.*[2] proposed a staggered A-type orbital ordering for this system based on their observations of the structural and magnetic phases at low temperature. A similar ordering was also proposed by Suzuki *et al.*[4]. Though the magnetic structure at low temperatures has been unambiguously established by the above mentioned experiments, there has not yet been any experiment such as X-ray resonant spectroscopy to directly probe the orbital order. Determination of exchange couplings using neutron scattering techniques by Chung *et al.*[5] is in apparent contradiction with the proposed staggered A-type orbital ordering. As pointed out by these authors, the proposed orbital order in Refs. 2,4 lacks the consideration of trigonal distortion, which is found to be strongest in MnV_2O_4 among all the vanadium spinels. The trigonal distortion has often shown to have significant effects on the orbital order[6,7].

In this Letter we show, based on density functional theory (DFT) calculations, that the ground state tetragonal space group symmetry at low temperatures is $I4_1/a$ and strongly driven by correlation effects. We propose an orbital ordering consisting of orbital chains running along the axes a and b with orbitals rotated by about $45°$ within each chain. This ordering favors a noncollinear arrangement of spins, as observed experimentally, which is a convincing indication of its existence.

For our DFT calculations we considered a combination of three different methods, namely: (a) plane wave-based method (b) linear augmented plane wave (LAPW) method and (c) muffin-tin orbital (MTO) based N-th order MTO (NMTO) method. Results were cross-checked among the three schemes in terms of total energy differences, density of states and band structures. Since first principles calculations take into account all structural and chemical aspects appropriately, we expect to

TABLE I: Energy-minimized structural parameters for MnV_2O_4 . Lattice constants were kept at the experimental value[3]. The LSDA+U optimized structural parameters show the O x-coordinate to be non-zero, signaling the change of space group symmetry to $I4_1/a$.

	LSDA	GGA	LSDA+U (U=4.5 eV)
Mn	0.0 0.25 0.125	0.0 0.25 0.125	0.0 0.25 0.125
V	0.0 0.0 0.5	0.0 0.0 0.5	0.0 0.0 0.5
O	0.0 0.0243 0.7392	0.0 0.0236 0.7394	0.0059 0.0244 0.7383

gain a better understanding of the nature of the structural phase transition and possible orbital ordering.

We first performed a structural optimization using the plane wave method as implemented in the Vienna Ab-initio Simulation Package (VASP)[8] and considered exchange-correlation functionals within LSDA, generalized gradient approximation (GGA) and LSDA+U[9] in order to investigate the relative stability between $I4_1/amd$ and $I4_1/a$ symmetries in MnV_2O_4 . We used projector augmented wave (PAW) potentials[10] and the wavefunctions were expanded in the plane wave basis with a kinetic energy cut off of 450 eV. Reciprocal space integration was carried out with a k-mesh of 6×6×6.

Optimization of the atomic positions[11] within LSDA as well as GGA assuming ferrimagnetic spin arrangements between Mn and V atoms gave us a ground state structure of $I4_1/amd$ symmetry where the tetragonal distortion is found to be substantially reduced compared to the experimental estimate[3]. In order to check the influence of electron-electron correlation on the structural optimization, which has been found to be important in previous reports[12], we have further optimized the atomic positions within the LSDA+U approach with different choices of U values[13] (U=0.5, 1, 2, 3, 4.5 and 6 eV) for both Mn and V. J was chosen to be 1 eV for all calculations. Remarkably, we observe that with the consideration of U beyond 2eV, the $I4_1/a$ symmetry becomes the ground state structure (see Table I). This optimized structure shows a tetragonal distortion close to the experimentally reported one[3]. These results indicate the importance of correlation effects for the description of the correct orbital ordering and the low temperature structure.

We analyzed the resulting orbital order with the full potential LAPW method as implemented in the Wien2k code[14]. The atomic sphere radii were chosen to be 2.01, 1.98 and 1.77 a.u. for Mn, V and O respectively. We chose the APW+lo as the basis set and the expansion in spherical harmonics for the radial wave functions was taken up to $l = 10$. The charge densities and potentials were represented by spherical harmonics up to $l = 6$. For Brillouin- zone (BZ) integrations we considered a 52 k points mesh in the irreducible wedge and the modified tetrahedron method was applied[15]. The collinear ferrimagnetic spin arrangements between Mn and V was taken the same as for the structural optimization cal-
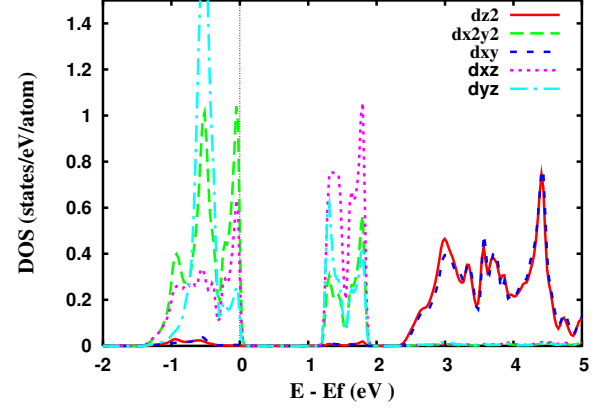

FIG. 1: (Color online) LSDA+U V-d partial DOS for U=4.5 eV in the APW+lo basis. Only the DOS for the majority spin channel is shown (the minority spin channel is unoccupied).
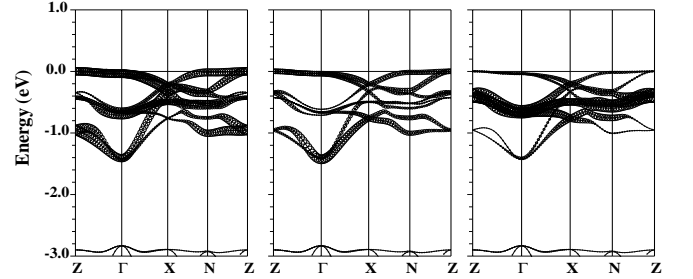

FIG. 2: LSDA+U bandstructure of MnV_2O_4 (APW+lo basis) projected onto V- x^2-y^2, xz and yz character (from left to right) in the energy range [-3 eV, 1 eV]. The high symmetry path of the tetragonal Brillouin zone was considered.

culations. In all further calculations we considered the LSDA+U approximation[16] and fixed the value of U at 4.5 eV which reproduces the experimentally observed orbital moment in vanadium, as will be discussed later.

In Fig. 1 we show the electronic density of states (DOS) calculated within the LSDA+U approximation. In the partial DOS one observes the usual t_{2g} (consisting of x^2-y^2, xz and yz orbitals defined in the crystallographic coordinate system)[17] and e_g (consisting of xy, $3z^2$) splitting of V d-orbitals due to the O octahedral crystal field. Inclusion of correlation effects in the V d-orbitals through the LSDA+U approach, splits the t_{2g} states further and opens a gap of 1.1 eV. The degeneracy between all the three t_{2g} orbitals is lifted in the low symmetry $I4_1/a$ group[18]. All t_{2g} orbitals are partially occupied with higher x^2-y^2 and yz occupancy compared to xz. This becomes more evident in the band structure results. Fig. 2 shows the t_{2g} bandstructure in the majority spin channel, which is separated from occupied O-p dominated bands by a gap of 1.5 eV and from unoccupied e_g-like bands by a gap of 0.2 eV. The fatness of the bands indicate the projected band characters of x^2-y^2, xz and yz orbitals.
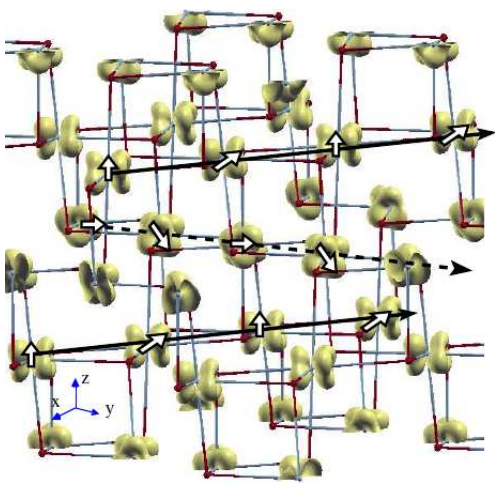
FIG. 3: (Color online) Three dimensional electron density plot showing the orbital ordering. The black solid and dashed lines designate the orbital chains. The arrows superimposed on the electron density at each V site, mark the rotation sense of the orbitals as one moves to neighboring V sites within a given chain. The atoms at the alternate corners of the distorted cubes are occupied by V and O respectively. The isovalue was chosen as 0.1 e^{-}/(Å^{3}).

Significant mixing of orbitals happens due to the low symmetry of the $I4_1/a$ space group. In Fig. 3 we show the three-dimensional electron density of occupied V t_{2g} orbitals on a real space grid. We identify a long range order pattern for the orbital distribution. Contrary to the proposed staggered A-type order[2,4], we observe orbital chains along a and b directions (indicated by solid and dashed lines) with the orbitals within each chain rotated alternatively by about 45° (shown by the arrows).

In order to assign the precise V orbital compositions we have performed NMTO-downfolding[19] calculations to construct a V-t_{2g}-e_g only low-energy Hamiltonian by integrating out degrees of freedom other than V-t_{2g}-e_g, starting with a full LSDA+U Hamiltonian. Diagonalization of the on-site energy block of this 5 x 5 Hamiltonian gives rise to eigenstates given by:

$$|1\rangle = .78|x^2-y^2\rangle - .59|xz\rangle - .21|yz\rangle + .07|xy\rangle + .02|z^2\rangle$$
$$|2\rangle = -.35|x^2-y^2\rangle - .15|xz\rangle - .92|yz\rangle - .09|xy\rangle - .07|z^2\rangle$$
$$|3\rangle = .52|x^2-y^2\rangle + .79|xz\rangle - .31|yz\rangle - .13|xy\rangle + .02|z^2\rangle$$
$$|4\rangle = .05|x^2-y^2\rangle - .08|xz\rangle + .11|yz\rangle - .66|xy\rangle - .74|z^2\rangle$$
$$|5\rangle = -.02|x^2-y^2\rangle - .11|xz\rangle + .04|yz\rangle - .73|xy\rangle + .67|z^2\rangle$$

with energies 0.81, 1.19, 1.47, 2.05, 2.28 eV respectively.

We observe that the lowest energy state has predominant x^2-y^2 character -which is expected due to the tetragonal distortion with the compression of VO$_6$ octahedron along the c-direction- with a significant mixing of xz character. The next higher energy state is dominated by yz character. Therefore, the second electron of V^{3+} always occupies the orbital with predominant yz charac-

ter in all V sites. The rotation of orbitals with respect to each other within the chain and between the chains (see Fig. 3), can therefore be explained due to the staggered trigonal distortion that is present both within the ab-plane and along the c-direction. Despite an apparent *antiferro-orbital* ordering, we call the ordering *ferro-orbital* since it is in all sites the same orbital that is occupied by the second electron, and not an alternating occupation of xz and yz.

The spin-orbit effect has been observed to play a significant role in dictating the nature of orbital order[6,20] in ZnV$_2$O$_4$ and was proposed to be important for the magnetic and orbital physics of MnV$_2$O$_4$ [21]. We performed LSDA+U+SO calculations with the same U values as mentioned above, where the spin-orbit effects have been introduced as a second variation using the scalar relativistic approximation. Contrary to the case of ZnV$_2$O$_4$[6], we do not observe any significant difference in charge density, from that of LSDA+U. The value of the orbital moment depends sensitively on U. The experimental V moment is best described for U=4.5 eV. At this U value we obtain an orbital moment of about 0.34 μ_B at V site which is antiparallel to the spin-moment (1.65μ_B). The total magnetic moment of 1.31 μ_B is close to the measured value[2] of 1.3 μ_B. Also, the calculated magnetic moment at the Mn site is found to be 4.24 μ_B in good agreement with the experimental estimate[2]. The orbital moment at the V site seems to develop an appreciable value only beyond a critical U value, U$_c$ (3.0 eV < U$_c$ ≤ 4.5 eV)[22], which may be interpreted as *Coulomb enhanced spin-orbit effect*[23].

We note that the perfect antiferro-orbital ordering as proposed by Refs. 4 and 2 would imply a quenching of orbital moment. The presence of a finite orbital moment can be associated with the breakdown of perfect antiferro-orbital ordering and may explain the domain alignment by magnetic field as observed by Ref. 4.

We have also computed the magnetic exchange couplings from first principles by considering LSDA+U total energy calculations with the PAW basis for different spin alignments of V atoms within the V tetrahedra. Mapping the total energies to a Heisenberg like model, we obtain exchange interactions along the orbital chains (J) of 11 meV and between the chains (J$'$) of 2 meV. This implies α = J$'$/J ≈ 0.2 compared to 0.3 found by Chung *et al.*[5]. Perfect antiferro-orbital ordering with xz and yz alternately occupied along the c-axis would however yield much smaller ratios of J$'$/J, since the overlap between orthogonal yz and xz orbitals at neighboring sites would have been nearly zero. The moderately strong value of J$'$, as obtained in the DFT calculation, originates from large mixing of different t_{2g} orbitals influencing the overlap of the renormalized orbitals at neighboring sites.

Our calculations described so far assume the collinear arrangement of V spins, while experiment reports a transition from collinear to noncollinear spin arrangements coincident with the structural phase transition. In order to check whether our proposed orbital order sustains

a noncollinear arrangement of V spins, we performed PAW calculations where we relaxed the V spin orientation keeping the Mn spins aligned parallel to the c axis[2]. The relaxed spin structure shows the V spins to be canted with respect to the c axis by about $63°$, which is in very good agreement with the experimentally estimated canting of $65°$[2]. The noncollinear spin arrangement was found to be slightly favoured over the collinear ferrimagnetic spin arrangement by an energy gain of 3 meV. Though this energy difference is almost within the accuracy limit of DFT, the good agreement between theory and experimental estimates is encouraging.

To conclude, we have carried out DFT-based first-principles calculations to investigate the nature of the orbital ordering in MnV_2O_4 which is closely associated with the transition from a high temperature cubic structure to a low temperature tetragonal structure. Our geometry-optimized structures for MnV_2O_4 show a strong influence of correlation effects in the choice of the *correct* low temperature structure. The obtained ground state structure, $I4_1/a$ looses the mirror and glide symmetry compared to the alternative proposed candidate $I4_1/amd$. The O in $I4_1/a$ are in 16f positions with nonzero x-coordinate, which makes the V-O bondlengths even in the ab-plane to be unequal. This lowering of symmetry necessarily breaks the degeneracy of the t_{2g} states completely and also introduces mixing between different t_{2g} states. The resulting eigenstates therefore turn out to be of *mixed-character* and *nondegenerate*, which get filled up by two V electrons. The occupied orbitals follow the site symmetry of vanadium which is 4-fold rotation times inversion to give rise to orbital chains with orbitals rotated with respect to each other both within and between the chains. Our DFT computed V-V magnetic coupling is found to be in agreement with the experimental findings[5]. These results provide an explanation of the controversy between *antiferro-orbital ordering* versus the strong exchange between orbital chains ($J^{'}$). We further showed that our proposed orbital ordering is capable of predicting correctly the noncollinear spin structure as observed experimentally[2]. Further experiments like X-ray resonant spectroscopy would be helpful to probe directly our proposed orbital order.

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[17] The crystallographic *ab*-plane is rotated by $45°$ from the basal plane defined by the V-O bonds, thereby forming t_{2g} states of x^2-y^2, xz and yz symmetry instead of more commonly used convention of xy, xz and yz.

[18] This is in contrast to the situation in $I4_1/amd$ symmetry where the degeneracy between xz and yz is maintained (see *e.g.* Fig.2 in Ref. 6).

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